



PATENT SPECIFICATION

DRAWINGS ATTACHED

1.189,221

Inventors: ARNOLD ISENBURG, WILFRIED PABST and GERD SANDSTEDE

Date of Application (No. 11235/67) and filing Complete Specification: 9 March, 1967.

Application made in Germany (No. B86168 VIb/21b) on 11 March, 1966.

Complete Specification Published: 22 April, 1970.

Index at acceptance:—H1 BF

International Classification:—H 01 m 27/04

COMPLETE SPECIFICATION

Metal Electrodes for Galvanic High-Temperature Fuel Cells

We, BROWN, BOVERI & COMPANY LIMITED, a corporation organised under the laws of the confederation of Switzerland, of Eaden, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to galvanic high-temperature fuel cells which include an oxygen-ion-conducting solid electrolyte, and which employ gases as fuels.

According to the invention, there is provided a galvanic fuel cell for use at elevated temperatures, comprising a solid electrolyte body of an oxygen-ion conducting material, and wherein the cell anode consists of copper or copper alloy impregnated within a porous surface layer of an oxygen-ion conducting material on said solid electrolyte body, the copper alloy having a main ingredient of copper.

It is surprising that a copper anode sticks satisfactorily to a solid electrolyte when the working temperature of the cell is only very little below the melting point of the metal. At this temperature copper experiences very considerable recrystallisation phenomena which should impair adhesion and therefore electrode activity, but no such impairment can be observed. Curves in which current density is plotted against voltage for copper anodes in a cell show that the anode sticks satisfactorily; also, no concentration polarisation can be observed, indicating that the combustion products can diffuse satisfactorily.

To form the anode a solid electrolyte having a porous surface is impregnated with a copper salt solution or melt, or with mixtures of a copper salt solution or melt and one or more alloy metal salt solutions or alloy metal salt melts which are subsequently reduced to copper or the alloys of copper. Copper must form the main ingredient of the metal phase of the alloys. Nickel, cobalt, manganese, chromium and silver can be used as alloy ingredients,

[Price 5s. 0d.]

The alloying enables the electrode vapour pressure at the working temperature to be lowered. Also, some alloy ingredients, such as nickel, help to increase the solubility of the hydrogen in the anode and thus increase the efficiency of the anode.

The drawing shows a voltage/current-density curve I of a high-temperature fuel cell; the curve was plotted at a temperature of 900°C with a copper electrode according to the invention as anode and a silver cathode. Hydrogen was used as combustion gas and oxygen as oxidising agent. Curve II was plotted in comparable conditions but with a conventional platinum anode. The current density is plotted along the abscissa in mA/cm² and the cell voltage in mV is plotted along the ordinate. After 300 hours operation at a current density of 300 mA/cm² there was no decrease in anode activity. This is very surprising, since the working temperature is so high in relation to the melting point of copper (1084°C) that a reduction in anode activity could be expected because of recrystallisation phenomena of the metal. If recrystallisation should prove disadvantageous after prolonged operation of the electrode, the anode can be regenerated quite simply by the copper being oxidised with pure oxygen or air, then reduced again. A regenerated anode has the same voltage/current-density characteristic as the curve I of the drawing.

The preparation of the above described anode will be described in the following examples.

EXAMPLE 1

To prepare the electrolyte, 2 g of a mixed oxide, comprising 92 mol % of zirconium oxide and 8 mol % of yttrium oxide, are charged into a 24 mm diameter mould and pressed smooth at a very low pressure of approximately 1 kp/cm². This layer is coated with 200 mg of an intimate mixture of 40% by volume of the same oxide powder with 60% by volume of ammonium carbonate and the whole

Cu anode

is pressed at high pressure (about 5 Mp/cm²) to form a tablet. The ammonium carbonate serves as a pore-forming agent and is decomposed without trace *in vacuo* at about 90°C for 1 hour. The moulding is baked at 1800°C for 3 hours, the porous layer becoming firmly sintered to the dense electrolyte layer. The porous electrolyte layer is impregnated with a saturated solution of copper nitrate, and the salt is roasted to form the oxide by being heated at 500°C. This step is repeated twice, with the result that the porous support layer receives an adequate quantity of copper oxide, so that after the oxide has been reduced to its metal, a porous conductive electrode is provided which forms the anode in the fuel cell. The reduction to the metal is performed in this cell by the action of the fuel gas.

EXAMPLE 2

The porous electrolyte layer whose preparation has been described in Example 1 is impregnated with a concentrated solution of a copper tetramine complex. Reduction of the salt to its metal leads to a conductive electrode, provided that the impregnation is repeated several times. As copper complex, there can be used, e.g., copper tetramine hydroxide in concentrated ammonia solution. Decomposition to the oxide is performed at about 400°C. Reduction to the metal is performed in the cell with the action of the fuel gas. As complex salts there can also be used those of the simple aliphatic amines, such as methylamine and ethylamine, and of amino acid with copper.

EXAMPLE 3

The porous electrolyte layer whose preparation has been described in Example 1 is impregnated with a mixture of saturated copper nitrate solutions and nickel nitrate solution. After removing the solvent the salts are decomposed to the oxide at 500°C and reduced to the metal alloy with hydrogen or some other reducing agent. The salt concentrations chosen are such that copper forms the main ingredient of the phase; one possible composition is 60% Cu, 40% Ni.

EXAMPLE 4

A copper-silver electrode is prepared in a manner analogous to that set forth in Example 3. The impregnated solid electrolyte is treated with hydrogen at about 400°C. After sintering in hydrogen at 900°C the electrode is ready for use.

Attention is drawn to our copending application numbered 11237/67 (Serial No. 1,189,222) in which is claimed other aspects of the process herein described.

WHAT WE CLAIM IS:—

1. A galvanic fuel cell for use at elevated temperatures, comprising a solid electrolyte body of an oxygen-ion conducting material, and wherein the cell anode consists of copper or copper alloy impregnated within a porous surface layer of an oxygen-ion conducting material on said solid electrolyte body, the copper alloy having a main ingredient of copper.

2. A fuel cell according to claim 1, wherein the body and the layer are formed from sintered particulate electrolyte material.

3. A fuel cell according to claims 1 or 2, wherein the materials of the porous surface layer and the solid electrolyte body are the same.

4. A fuel cell according to claims 1, 2 or 3, wherein the minor ingredient or ingredients of the copper alloy is or are selected from the group cobalt, nickel, manganese, chromium and silver.

5. A galvanic fuel cell according to claim 1 and having an anode produced by a process substantially as herein described in any one of the examples.

6. Process for the production of an anode of a galvanic fuel cell used at elevated temperatures, the fuel cell including a solid electrolyte body of an oxygen-ion conducting material, wherein a porous surface layer of an oxygen-ion conducting material on said solid electrolyte body is impregnated with a copper salt solution or melt, or a mixture of a copper salt solution or melt and an alloy metal salt solution or melt, and wherein the anode is formed by reducing the solution(s) or melt(s) to copper or copper alloy.

7. Process according to claim 6, wherein prior to the impregnation step a body of particulate electrolyte material has formed thereon a layer consisting of a particulate mixture of electrolyte material and a pore forming agent, where the body and layer thereon is first pressed, and then sintered to provide a sintered body in which the pore forming agent is decomposed to provide a porous surface layer.

8. Process for the production of an anode of a galvanic fuel cell used at elevated temperatures, substantially as herein described in any one of the examples.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.

1189221

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

